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High Pressure Research

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Abstract

We describe a method for precisely etching small cavities into the culets of diamond anvils for the purpose of providing thermal insulation for samples in experiments at high pressures and high temperatures. The cavities were fabricated by using a highly directional oxygen plasma to reactively etch into the diamond surface. The lateral extent of the etch is precisely controlled to micron accuracy by etching the diamond through a lithographically fabricated tungsten mask. The performance of the etched cavities in high-temperature experiments in which the samples are either laser-heated or electrical heated is discussed.

Keywords: plasma etching, high temperature, laser heating, lithography, designer anvils.

1. Introduction

The study of the physical properties of materials under conditions of extremely high pressures combined with very high temperatures is a very active area of research, with relevance to geophysics and planetary science as well as to important topics in physics, chemistry, and materials science [i,ii,iii,iv,v,vi]. To investigate materials under static pressures of up to several Mbars, diamond anvil cells (DAC's) have been proven to be very successful devices. However, many problems arise when attempting to perform experiments under conditions of both high pressure and high temperature. Because diamond starts to rapidly graphitize at temperatures above about 1000 ˚C, heating of the entire diamond anvil cell is limited to about this temperature. To reach higher temperatures, heating must be focused on just the tiny sample inside the diamond anvil cell (typically, by using a high-power laser) while the rest of the diamond anvil cell is kept at a relatively low temperature.

An essential feature of these focused heating techniques is the introduction of a layer of thermal insulation around the sample to allow its temperature to be decoupled from that of the rest of the DAC. Many of the problems associated with high temperature DAC experiments are related to the properties and behavior of this insulating layer under high pressures. The insulating layer must satisfy a number of requirements: it must have a sufficiently low thermal conductivity; it must be chemically inert and not react with the sample under very high temperatures; it should also be highly uniform in thickness in order to ensure good temperature uniformity throughout the sample; finally, it should have good optical and x-ray transparency to allow for spectroradiometric temperature measurement, laser heating of the sample, and the application of optical and x-ray diagnostics to the sample. Materials such as Al_2O_3, NaCl, or MgO powder and various inert media (e.g., neon, helium, argon) are commonly used insulators [vii,viii].

Because pressurization of the DAC almost invariably involves considerable plastic deformation of the sample/insulator assembly, high-temperature experiments are problematic despite careful preparation and placement of the sample and insulating layers in a DAC. For example, the temperature uniformity of the sample can be affected by the development of nonuniformities in the insulator thickness. Furthermore, due to the thinning of the insulating layer, increasingly higher pressures usually require increasing amounts of laser heating power in order to maintain the same target temperature. Therefore, it is desirable that the insulating layers have uniform thickness and maintain their shape and thickness as much as possible under high-pressure conditions.

2. Experimental

Etched Cavities in Diamond Anvils

Our approach to maintaining DAC thermal insulating layers of uniform thickness and fixed shape is to embed the insulating layers in cavities etched into the diamond anvils themselves. Figure 1 shows a schematic diagram of the DAC sample/insulator assembly. The thermal insulating layers (e.g., Al_2O_3 powder, NaCl powder) are packed into cavities in the culets of the diamond anvils, which provide very rigid lateral and axial support for the insulating layer, essentially trapping the insulator and limiting its ability to plastically flow and deform under pressure loading.

Fabrication of the Etched Cavities

Shallow, circular cavities in the culets of the diamond anvils were fabricated using a combination of optical projection lithography, tungsten sputter deposition, and oxygen plasma etching. In order to delineate the diamond area to be plasma etched, we first fabricated a plasma-resistant mask on the diamond surface using lithography. Since standard polymer photoresists are etched very rapidly by an oxygen plasma [ix], we first fabricated a photoresist mask which in turn was used to make a plasma-resistant tungsten mask on the surface of the diamond anvil. After completion of the oxygen plasma etching process, this tungsten mask can be easily removed by acid etching.

To fabricate etched cavities, we first deposited a film of positive photoresist (Clariant AZ1518) approximately 1 μm thick onto the culet of a diamond anvil. The entire diamond anvil was then exposed to ultraviolet light using a projection aligner (Canon FPA-141F) except for a small circular area of the photoresist 30 to 90 μm in diameter at the center of the culet. After processing the photoresist with a developer and washing away the exposed photoresist, only a 30-90 μm diameter circular region at the center of the culet remained covered with photoresist. Finally, a film of tungsten 0.5 μm thick was deposited onto the anvil, and the remaining photoresist was washed away with acetone. The resulting tungsten mask covers the entire surface of the diamond anvil except for the 30-90 μm diameter circular region which is directly exposed to the oxygen plasma.

To etch the diamond, a 13.56 MHz rf-driven, hollow-cathode plasma source, custom designed by Lawrence Livermore National Laboratory, was used. This source generates a high-density oxygen plasma jet with a plume diameter of approximately 3 mm, and can achieve an etch rate of up to about 10 μm/hr at an rf power of 27 Watts as the exposed diamond chemically reacts with the oxygen plasma to form volatile products such as CO and CO_2 which are abstracted away from the diamond surface [x]. An attractive feature of our plasma jet etching process is that it is highly directional and so the lateral shape and dimensions of the etched cavity conform precisely to those of the tungsten mask. In this way, we can precisely etch features into diamond with a lateral resolution of 1 μm, the current resolution of our optical lithography process. In contrast to our plasma jet etching process, much more isotropic plasma etching conditions are obtained if a large-area discharge is used to generate the plasma [x].

Our process also allows for very precise control over the cavity depths. Prior to the actual plasma etching run on the diamond anvil, calibration etching runs are performed on other diamond substrates in order to measure the etching rate. We then use this measured etch rate to calculate the etching time required to reach the desired target depth. By this method we can routinely etch to a depth accuracy of less than 1 μm.

Cleanliness of the diamond surface is extremely important in order to etch cavities having smooth, optically transparent surfaces. The presence of even small amounts of tiny, residual surface impurities on the diamond surface can lead to a cavity having a very rough surface texture with a large number of spike-like features. These rough surface textures result from the surface impurities masking portions of the underlying diamond surface from the oxygen plasma. To remove these surface impurities, the surface was first wet wiped with acetone and methanol, and then subjected to a nonspecific argon-ion rf-discharge etch prior to starting the reactive oxygen plasma etch. Because of the higher operating energy of the argon-ion etch (≈300 eV) compared to the oxygen etch (≈25 eV), the argon-ion etch is much more effective at cleaning the diamond surface of surface impurities. Figure 2 shows a scanning electron micrograph (SEM) of a diamond anvil which had a 90 μm diameter, 8 μm deep cavity plasma etched into the culet.

Etched Anvils with Laser Heating

To test the ability of our etched anvils to contain thermal insulating layers while transmitting large incident laser fluxes and withstanding large diamond anvil stresses, we used these anvils to perform a set of laser-heating experiments using tantalum as the sample and NaCl as the thermal insulator. NaCl was packed into the cavities by gently squeezing the dried NaCl between a diamond anvil with an etched cavity and a standard diamond anvil with a 300 μm flat culet. For out initial experiments, we mounted only one anvil with an etched cavity into the DAC, with the opposite anvil being a standard anvil with a 300 μm flat culet. In this way, we were able to directly compare the amount of laser power required for the heating the sample through the two different anvils.

Our double-sided laser heating experiment was performed at beamline 13ID-D at GSECARS (Advanced Photon Source, Argonne National Laboratory, IL) which utilizes two diode-pumped ytterbium fiber lasers with output power up to 100 Watts each [xi]. Heating experiments were performed to pressures up to 56 GPa and temperatures over 3500K with no apparent damage to the etched anvil, demonstrating that the etched cavity surface of the anvil was sufficiently transparent to transmit the high-power laser beam to the sample without harm to the anvil. During the course of the experiment, we observed that for a given sample temperature about 20% to 40% less laser power was required for the laser directed through the anvil with the plasma etched cavity than for the laser directed through the opposing anvil, which supports the view that the etched cavity is effective at maintaining a thick insulating layer even under very high pressures. Figure 3 shows images of the plasma etched cavity taken with a Veeco optical profilometer after cleaning out the etched cavity at the end of the experiment. The images show that the cavity depth is very uniform with a variation of only $\pm$0.1 μm or about 1.5% over most of the surface area of this 6.7 μm deep cavity.

Etched Anvils with Internal Resistive Heating

Etched anvils have also been successfully used to contain thermal insulating layers for internal resistive heating experiments, in which a small heating element and the sample are electrically heated to very high temperatures [xii]. Figure 4 shows a schematic diagram for this type of experiment. In this case, a cavity was etched into the culet of a "designer" diamond anvil with eight thin-film tungsten probes which were lithographically fabricated on a diamond anvil and then encased in a layer of high-quality, epitaxially deposited CVD diamond. The cavity was etched after completion of the lithographic patterning of the electrical probes and the deposition and polishing of the CVD diamond layer. The cavity was 35 μm in diameter, 8 μm deep, and packed with 0.25 μm alumina powder for thermal insulation. A tungsten heating element 10 μm wide and 0.5 μm thick was then lithographically fabricated on top of the alumina layer. Several experiments with gold samples have been performed to pressures of 21 GPa and temperatures of nearly 2000 K, and this design has been successfully used to pressures of 50 GPa and temperatures of 2900 K. The fact that the thin-film electrical heater is able to function at these pressures and temperatures indicates that a sufficiently thick layer of thermal insulation is maintained at high pressures, and that there is very little plastic flow of the alumina contained in the cavity since even small amounts of plastic flow can easily damage or destroy the very thin (0.5 μm thick) tungsten heating element on top of the alumina layer.

3. Discussion

The plasma etching of shallow cavities into the culets of diamond anvils for the purpose of inserting a thermal insulation layer between the sample and the diamond anvils has been found to be an attractive approach for performing very high temperature DAC experiments using either laser heating or internal resistive heating. Plasma etching offers extremely precise control over the dimensions of the cavity to micron accuracy, both in depth as well as in the lateral directions. The highly directional nature of the plasma etching process ensures that the shape of the cavity precisely matches that of the tungsten mask, with minimal undercutting of the mask. Although the cavities that we have etched thus far have depths of less than 10 μm, there are no apparent obstacles to etching much deeper cavities by extending the etching time.

The quality of the finish of the etched cavities appears to be very high. In contrast to ion-milling or sputtering, which rely on momentum transfer with high-energy ions to remove material, reactive ion etching with an oxygen plasma uses relatively low energy ions (≈25 eV as opposed to ≈300 eV or more for ion milling), and therefore tends to be a more "gentle" process for removing material. This is a very attractive feature for the machining of diamond anvils since the formation of microcracks and other defects during machining can be expected to weaken the anvils and limit their maximum achievable pressures. Based on our close visual inspections of the diamond anvils after oxygen plasma etching, we see no evidence that any microcracks or other defects are introduced into the anvils during plasma machining. The bottoms of the cavities are optically smooth and transparent and, and are able to transmit laser fluxes exceeding 10 Watts through the cavity surface during laser heating experiments.

4. Conclusion

In summary, the technique of placing thermal insulating layers into tiny cavities etched into the culets of diamond anvils appears to be a very attractive method for ensuring good, stable insulation of high-pressure, high-temperature DAC samples. There has been no apparent evidence of any noticeable plastic flow or thickness change in any of the thermal insulators that we have placed into the diamond anvil cavities. We believe that this method of integrating thermal insulation layers into diamond anvils will prove useful for future efforts to achieve higher temperatures and pressures with diamond anvil cells.

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Figure Captions

Figure 1.

Schematic diagram of a diamond anvil cell assembly in which cavities have been etched into the culets of the two diamond anvils in order to contain thermal insulating layers. Typical dimensions for the etched cavities are 30-90 μm in diameter and 10 μm deep. The configuration shown is for a double-sided laser heating experiment.

Figure 2.

SEM micrograph of a diamond anvil with a 90 μm diameter, 8 μm deep cavity etched into the center of the 200 μm diameter culet.

Figure 3. Optical profilometer pictures of the 90 μm diameter, 8 μm deep cavity taken after high pressure laser-heating experiments.

(a) Contour plot showing the depth of the 90 μm diameter cavity as a function of position.

(b) Contour plot of the same cavity taken at higher depth magnification.

(c) 3D plot generated by the optical profilometer showing the bottom of the cavity.

Figure 4.

Schematic diagrams of a microheater designer diamond anvil assembly.

(a) A side-view of the assembly showing the designer anvil with a cavity 6-8 μm deep and 30-35 μm in diameter etched into the center of the culet. This cavity is filled with alumina, which provides thermal insulation for the electrical microheater on top of it.
(b) A top-view schematic of the microheater assembly, showing the alumina filled cavity and the tungsten microheater element that is fabricated onto it. Electrical current for the microheater is provided by the diamond embedded electrodes of the designer anvil.

Figure 1

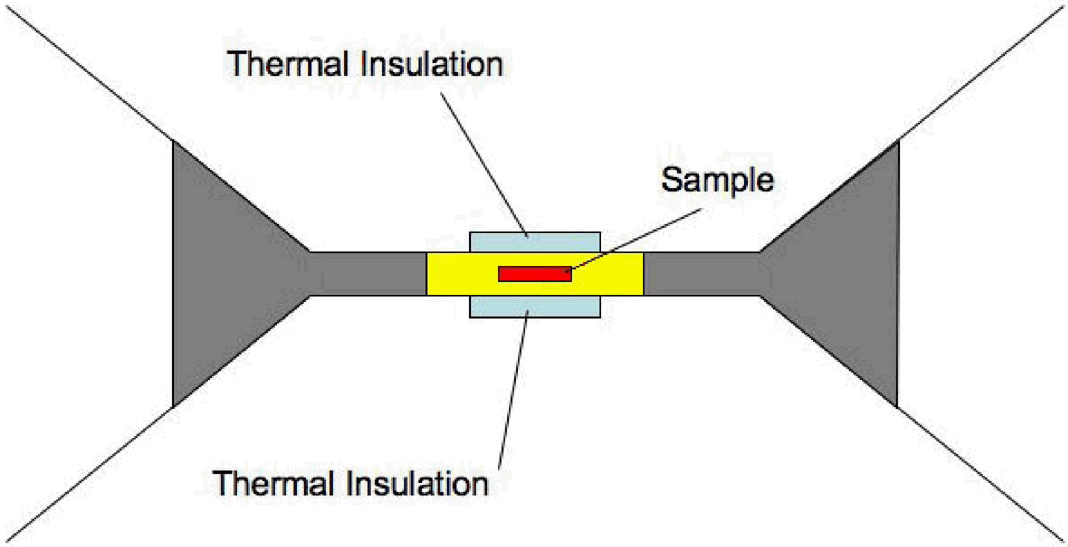


Figure 2

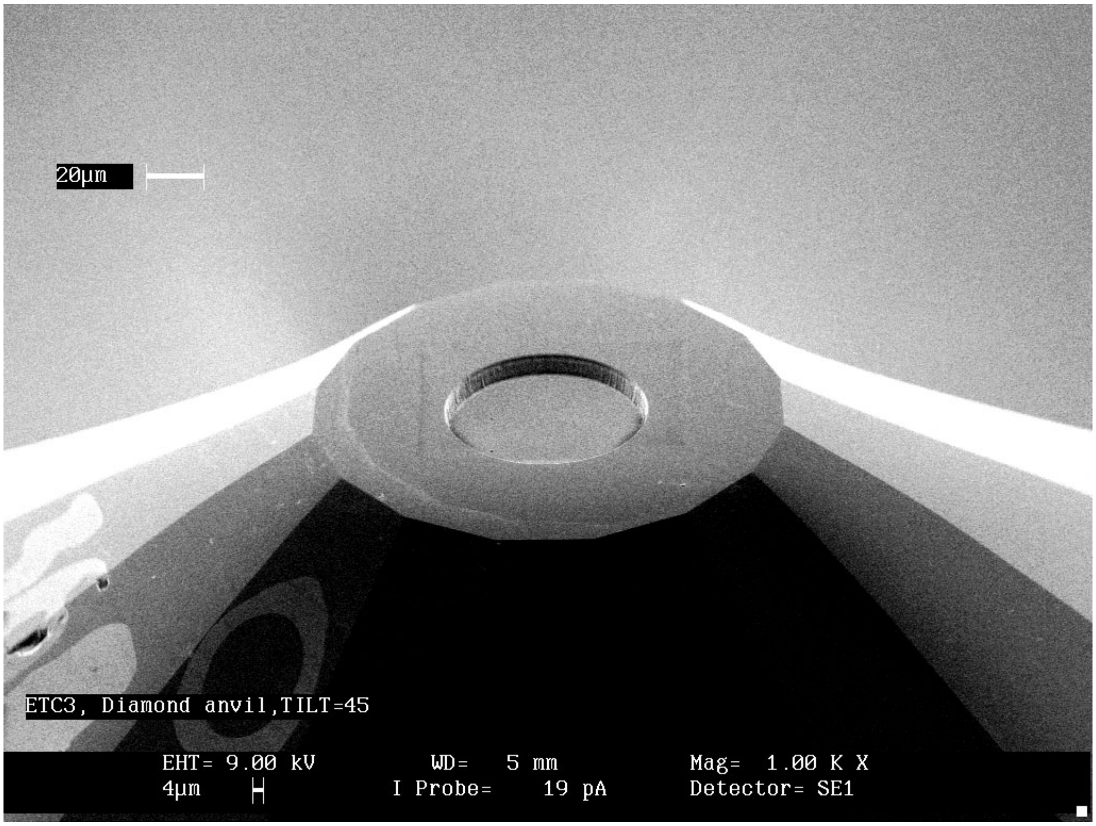
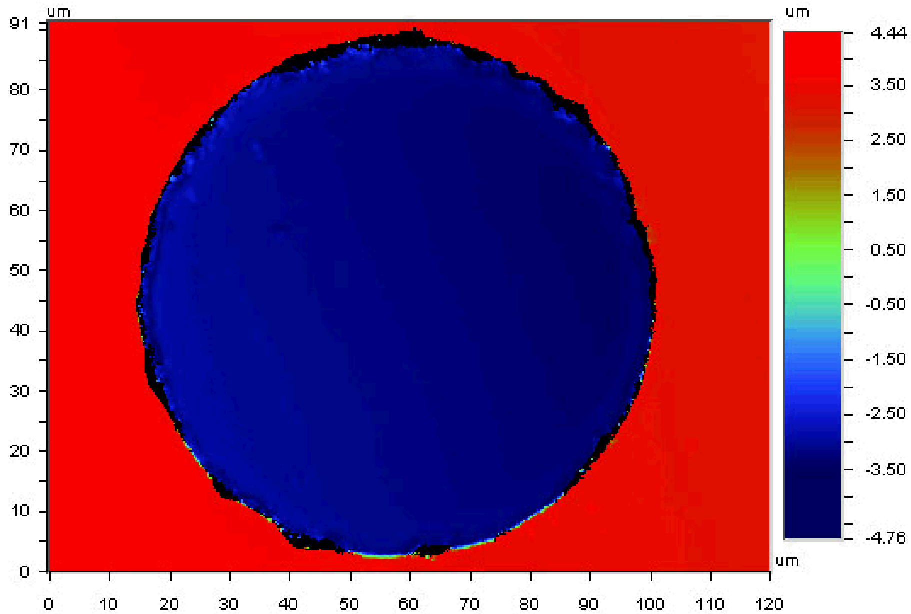

20µm
ETC3, Diamond anvil,TILT=45
EHT= 9.00 kV
WD= 5 mm
Mag= 1.00 K X
4µm
I Probe= 19 pA
Detector= SE1

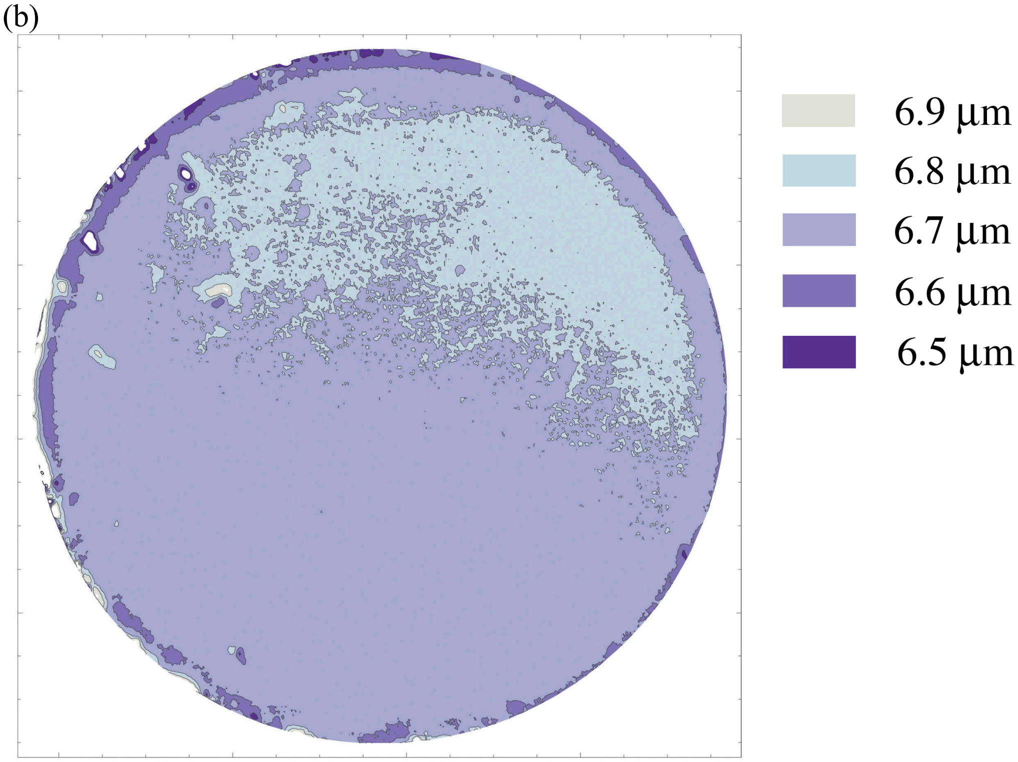
Figure 3

(a)



um
91
80
70
60
50
40
30
20
10
0
0 10 20 30 40 50 60 70 80 90 100 110 120
um
4.44
3.50
2.50
1.50
0.50
-0.50
-1.50
-2.50
-3.50
-4.76
um

(b)



6.9 µm
6.8 µm
6.7 µm
6.6 µm
6.5 µm

(c)

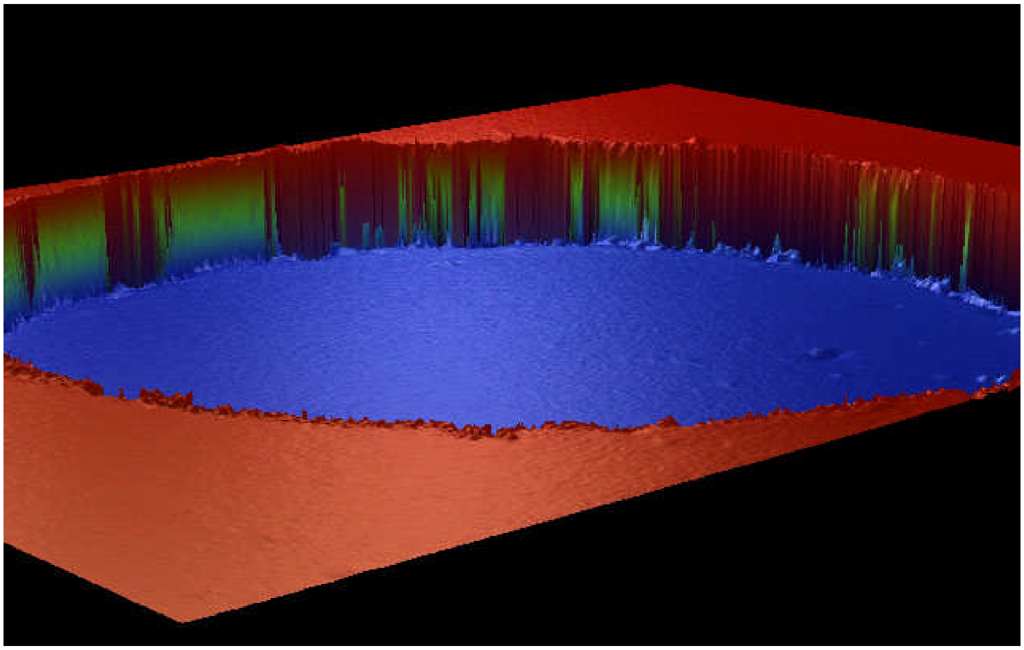
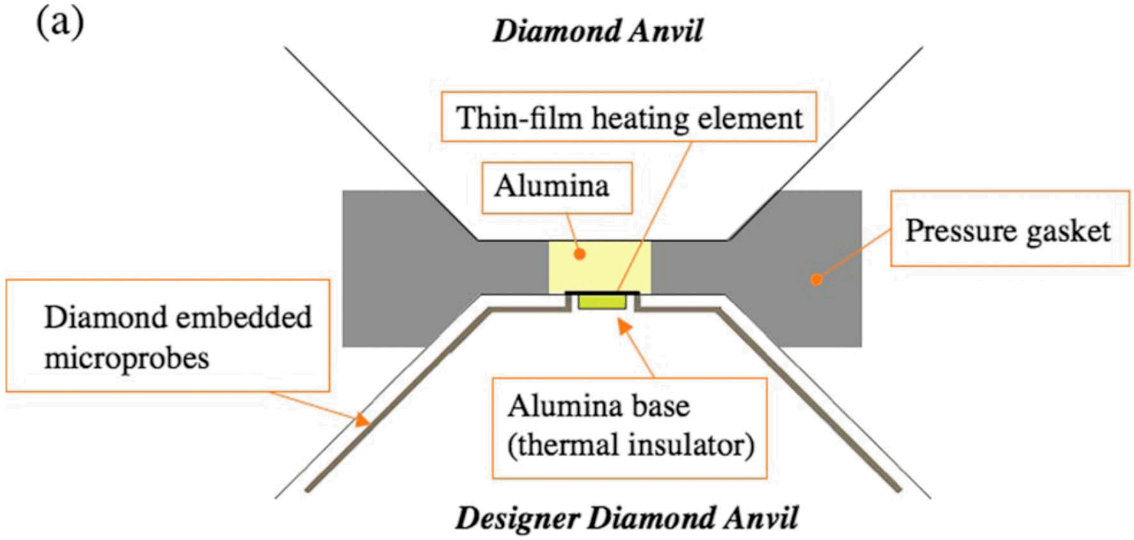
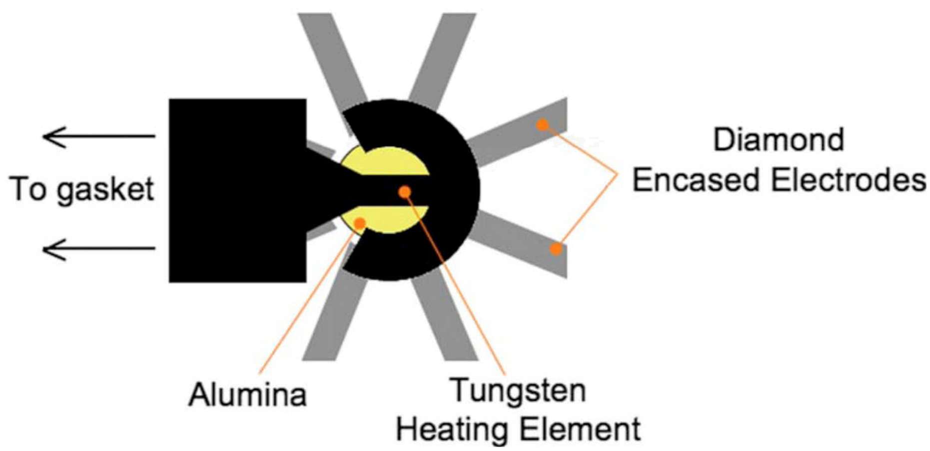


Figure 4

(a)


Diamond Anvil
Thin-film heating element
Alumina
Pressure gasket
Diamond embedded microprobes
Alumina base (thermal insulator)
Designer Diamond Anvil

(b)


To gasket
Diamond Encased Electrodes
Alumina
Tungsten Heating Element